AD-A132 044 RADIOLYSIS OF RESIST POLYMERS IV 1/1
POLY(P-SUBSTITUTED-ALPHA-METHYLSTYRENES)(U)
MASSACHUSETTS UNIV AMHERST MATERIALS RESEARCH LAB
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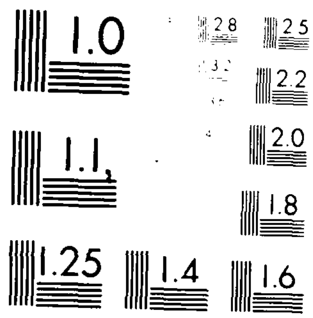

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The effect of saver-substituent on the radiation chemistry of poly(α-methylstyrene) (PMS) was compared for the fluoro (PFMS), chloro (PCMS), bromo (PBMS) isopropyl (PIPMS) and methoxy (PMEOM) derivatives. The radiolysis yields, ESR spectra and GC-MS analysis of products were obtained. PMEOMS and PIPMS gel readily by gamma-radiation. They may be useful as negative resist materials.

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Contract N00014-81-K0611

Task No. NR 056-773

TECHNICAL REPORT NO. 4

Radiolysis of Resist Polymers. IV.

Poly(p-substituted-α-methylstyrenes)

By

G.N. Babu, P.H. Lu, S.L. Hsu, and James C.W. Chien

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University of Massachusetts
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August 1983

Radiolysis of Resist Polymers IV Poly(p-substituted-α-methylstyrenes)

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Abstract

The effect of para-substituent on the radiation chemistry of poly(α-methylstyrene) (PMS) was compared for the fluoro (PFMS), chloro (PCMS), bromo (PBMS), isopropyl (PiPMS), and methoxy (PMeOM) derivatives. The radiolysis yields, ESR spectra and GC-MS analysis of products were obtained. PMS and PFMS have similar low radiolysis yields, products, and product distributions. Only main chain radicals were observed which persists up to near 200°. PCMS has increased values of $\underline{G}_s$, $\underline{G}_x$ and $\underline{G}_r$. The product analysis results suggest the presence of chlorine contributes to the primary process by dissociative electron capture and enhances the cleavage of the α-methyl group. Irradiation of PBMS caused crosslinking and yielded little volatile products. PMeOMS and PiPMS gel readily by γ-irradiation. They may be useful as negative radiation resists.

Introduction

High energy radiation produces profound changes in the structure of polymeric materials. The changes in the structure by radiolysis has been attributed variously to the steric, polar, and resonance effects.[2] As part of a search for improved polymeric electron beam positive resists, we have been interested in the propensity of polymers to undergo scission upon exposure to ionizing radiation. The effects of heavy atom substituents on the increase of chain scission yield without causing crosslinking have been reported.[3-5] Many halogenated derivatives of methacrylates exhibit this desirable property.

There have not been as great interest in negative E-beam resist probably because the cross-linked polymer due to irradiation is usually swollen by the solvent for unirradiated polymer causing loss of sharpness in contrast. Some of the polymers which have been investigated for negative lithography were p-substituted polystyrene[6], copolymers of styrene and glycidyl methacrylate,[7] iodinated polystyrenes,[8,9] chlorinated polystyrene,[10] and chloromethylated polystyrene.[11] The central purpose of this paper is to report the radiolysis results of poly(α-methylstyrene) and it para-substituted derivatives. The abbre-

viations used are PMS, PFMS, PCMS, PBMS, PMeOMS and PiPMS for poly(α-methylstyrene), poly(p-fluoro-α-methylstyrene), poly(p-chloro-α-methylstyrene), poly(p-bromo-α-methylstyrene), poly(p-methoxy-α-methylstyrene) and poly(p-isopropoyl-α-methylstyrene), respectively.

Experimental

The synthesis of the monomer have been reported elsewhere,[12] as are the procedures of cationic polymerization initiated by $SnCl_4$ and a cocatalyst. Molecular weights are determined by GPC. The method of γ-irradiation and calculation of G_s and G_x from $\overline{M}_n$ and $\overline{M}_w$ dependence on radiation dose, quantitative ESR, and GC-MS analysis of the volatile products were described in the previous papers of this series.[3-5]

Results and Discussion

Radiolysis yields

Most of the polymers have molecular weights sufficiently high for

Table 1

microlithography purpose. They are summarized in Table I. Two samples each of different molecular weights were synthesized for PFMS and PCMS. The polymerization of iPMS and MeOMS, however, led to products much

Table I. Initial molecular weights of p-substituted α-methylstyrene polymers

Polymer	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
PMS	3.1	5.9	1.9
PFMS (i)	1.7	2.4	1.4
PFMS (ii)	3.3	5.0	1.5
PCMS (i)	5.0	6.3	1.25
PCMS (ii)	3.3	4.0	1.2
PBMS	3.95	6.1	1.5
PiPMS	0.15	0.37	2.5
PMeOMS	0.53	1.31	2.45

lower in molecular weights than the others.

The values of G_s and G_x were calculated from the plots of $\overline{M}_n^{-1}$ and $\overline{M}_w^{-1}$ versus dose (D) shown in Figures 1-4. The results are listed in Table II. Also shown are the G_r values which is obtained from quantitative ESR for number of radicals produced per 100 eV. The results show only PFMS to have no tendency for crosslinking. PMS and PCMS have non-zero values for G_x. In the case of PBMS, though the polymer is soluble after irradiation, G_s-G_x has negative values indicating crosslinking. Irradiation of PMeOMS and PiPMS at low dose led to insoluble gels. Among the various polymers only PCMS has some tendency toward scission. All the other polymers have very low G_s values implying stability toward radiolysis. This may be attributed to the fact that the superexcited states produced upon interaction with the secondary electrons can decay by radiative or non-radiative processes *via* the manifolds of excited singlet and triplet states.

Fig. 1-4

Table II

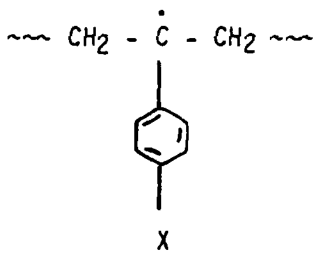
Table II. Radiolysis yields of p-substituted α-methylstyrene polymers

Polymer	G_s-G_x	G_s	G_x	G_r
PMS	0.33	0.39	0.06	0.20
PFMS (i)[a]	0.1	0.1	0	-[b]
PFMS (ii)[a]	0.2	0.2	0	0.22
PCMS (i)[a]	1.0	1.3	0.33	-[b]
PCMS (ii)[a]	0.8	1.0	0.20	1.21
PBMS	-0.15			0.018
PMeOMS	gel[c]			
PiPMS	gel[c]			

[a]i and ii refer to different preparations of the polymer of different molecular weights; [b]ESR spectra could not be integrated; [c]the polymer geled at very low dose.

Electron spin resonance

Fig. 5 Table III The ESR spectra of irradiated polymers are all centered near free electron g values, with symmetric line shape, and poorly resolved hyperfine splitting. Figure 5 shows the spectra and Table III gives the hyperfine parameters. The proton hyperfine splittings of the aromatic protons were poorly resolved in irradiated PMS and PFMS. In the latter case the fluorine hyperfine splitting was not resolved. The spectra of PCMS and PBMS have no resolvable splitting from the aromatic protons probably due to quadruple broadening by the Cl and Br atoms. From the spectra, the radicals are interpreted to be those of the main chain radicals (I):



X = H, F, Cl, Br

(I)

Fig. 6 The assignment is supported by the fact that the radicals survive excessive heating (Figure 6). In the case of PMS and PFMS the radicals persist to near or even above their T_g of 179° and 184°, respectively. The radicals in irradiated PBMS disappeared at ca. 120° which is 100° below its T_g of 220°.

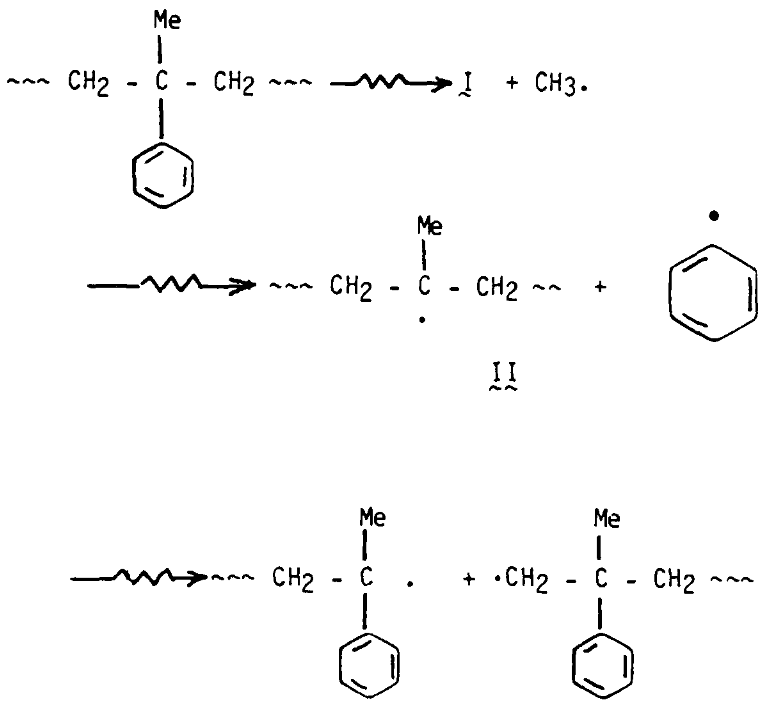
Table III. ESR parameters

Polymer	Hyperfine splitting, Gauss	
	alipatic protons	aromati[illegible]ons
PMS	12.8 (4H)	6.4 (2 *ortho* H, 1 *para* H)
PFMS	18G (4H)	9.0 (2 ortho H)
PCMS	15.5 (4H)	---[a]
PBMS	12.5 (4H)	---[a]

[a] not resolved.

Gas Chromatography-Mass Spectrometry and Radiolysis Mechanism

A. Poly(α-methylstyrene).-The relative ion current of volatile products from irradiated PMS are: CH_4 (1.0), C_2H_6 (1.2), C_3H_4 (6.7), C_3H_6 (1.8), C_3H_8 (2.7), C_4H_4 (22), C_4H_{10} (9.9), cyclopentendiene (6.1), C_6H_6 (72.8), $C_6H_5CH_3$ (20), $C_6H_5CH{=}CH_2$ (50.5), $C_6H_5C(Me)CH_2$ (184), and $C_6H_5C_3H_7$ (10). Three primary radiolysis events may be envisualized.



(1)

(2)

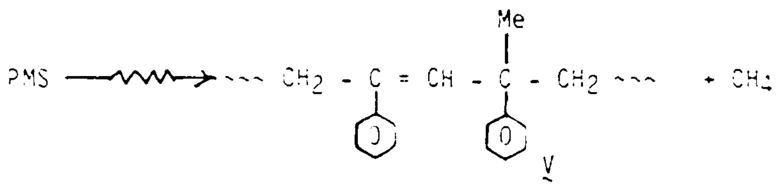
II

(3)

III IV

The methyl radicals led to CH_4 and other aliphatic hydrocarbon products. The phenylradicals produces benzene, toluene etc. Monomer can be cleaved from radicals III and IV.

There may also be molecular radiolysis processes such as:



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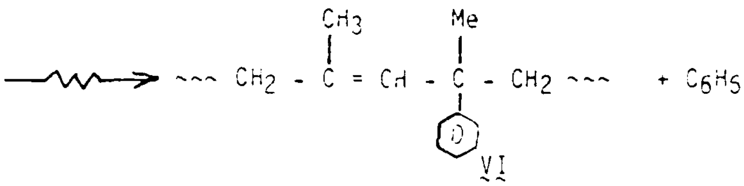
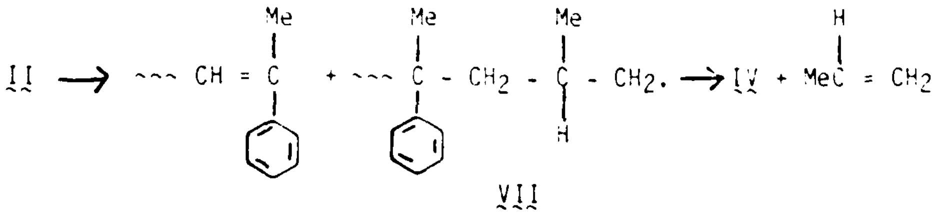


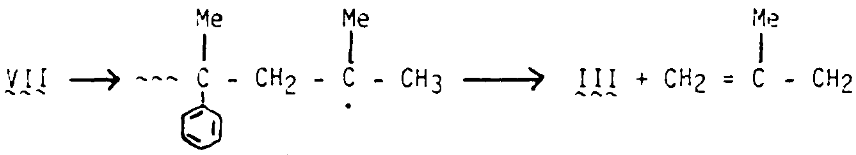
(5)

Combination of radicals I and II if they are in close proximity or their addition to V and VI result in crosslinks. On the other hand, reaction of the terminal radicals III and IV lead to chain extension and long chain branching either when III reacts with IV, or their reactions with radicals I or II or the double bonds of V and VI.

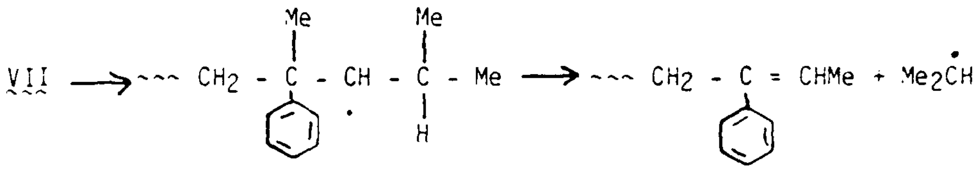
Main chain radical I was observed by ESR but not the main chain radical II. The latter is probably the source of saturated and unsaturated hydrocarbons.

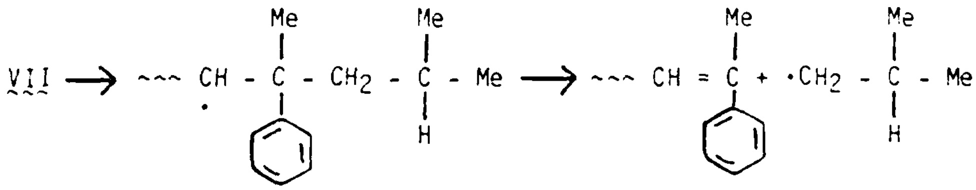


(6)

 (7)

VIII

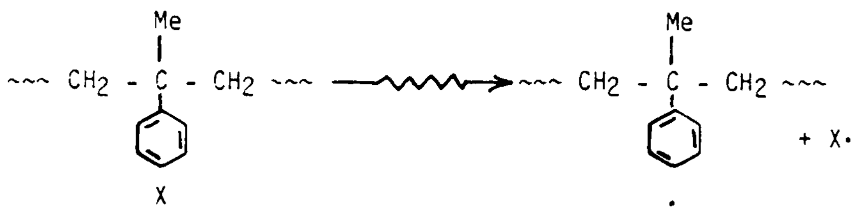
 (3)

 (9)

Abstraction of hydrogen by the propyl and butyl radicals forms propane and butane, respectively. The above mechanism accounts for most of the products observed as well as the ESR and scission and crosslinking results.

B. Poly(p-halo-α-methylstyrenes)

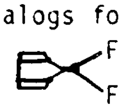
Radiolysis of p-halo-α-methylstyrenes can cause dissociative electron capture of the halogen atoms,



(10)

IX

in addition to the primary processes 1 - 3.

In the case of PFMS, G_s is smaller than that of PMS and there is no crosslinking. The hydrocarbon radiolysis products of the two polymers are quite similar. The relative ion currents of products from PFMS are: CH_4 (0.4), C_3H_4 (3.0), C_3H_6 (0.6), C_3H_8 (0.8), C_4H_4 (3.5), and C_4H_{10} (6.0). In addition, there were a large number of fluorine curtain proucts corresponding to the proton analogs for PMS: C_3H_7F (3.2), C_4H_3F (6.0), C_4H_9F (14.5), C_5H_5F (7.3), (38.9), C_6H_5F (29), $FC_6H_4CH_3$ (23), $FC_6H_4CH{=}CH_2$ (6.45), $FC_6H_4C(Me){=}CH_2$ (175.5) and $FC_6H_4C_3H_7$ (11.5).

Since the G_r values are nearly the same for PMS and PFMS, process 10 is probably not of great significance. The scission and

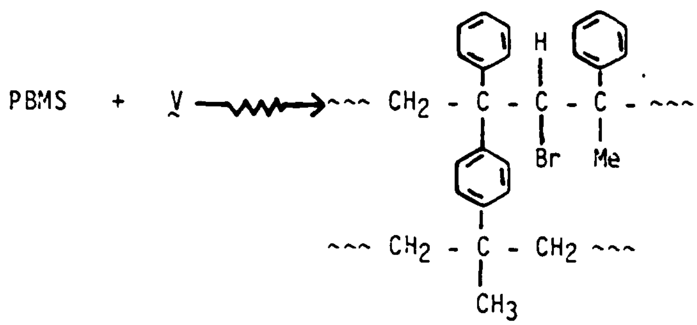
crosslinking yields are small and similar for the two polymers. It seems that the fluoro-substituent does not exert strong influence on reactions 1-3.

PCMS has larger $\underline{G_r}$, $\underline{G_s}$ and $\underline{G_x}$ yields than PMS and PFMS. The GC-MS analysis of radiolysis products show the ion currents: CH_4 (12.9), C_2H_6 (21.8), C_3H_6 (13.6), C_3H_8 (10.5), C_4H_{10} (61) for aliphatic hydrocarbon which are greater than that from PMS and PFMS. Furthermore, non-aromatic chlorides are also formed in quantities larger than similar fluorides from radiolysis of PFMS: HCl (4.2), CH_3Cl (17.4), C_3H_4Cl (20), C_2H_5Cl (28.1), C_3H_7Cl (3.3), CH_2Cl_2 (9.9). On the other hand the yields of aromatic chlorides are much reduced by comparison: C_6H_5Cl (3.0), $ClC_6H_4CH_3$ (0), $ClC_6H_4Cl{=}CH_2$ (1.5), $ClC_6H_4C(Me){=}CH_2$ (12.5).

The above results showed that the dissociative electron capture reaction 10 is an important primary process, and that the chlorine apparently promotes eq. 1 as well. On the other hand, the very low yield of chlorobenzene and the absence of p-chlorotoluene imply that reaction 2 is relatively unimportant. Finally, the chlorine substituent apparently suppresses the unzipping processes as the chloro derivatives of α-methylstyrene and styrene are found only in very small amounts.

The GC-MS of volatile products from irradiated PBMS are strange. The few identifiable products, CH_4, C_2H_6 and C_3H_8 are minute in quantities. The most abundant species with mass numbers 83 and 85 cannot be assigned. There was no evidence for either HBr or CH_3Br. A

possible explanation is that the bromine substituent promotes reaction 4. Then dissociative electron capture of a nearby molecule results in crosslinking as depicted by



(11)

C. Poly(p-methoxy-α-methylstyrene) and poly(p-isopropyl-α-methylstyrene)

PMeOMS and PiPMS behave similarly toward γ-radiation giving products summarized in Table IV which indicate the occurence of reactions 1 and 4 to 9. Since there were no monomers produced, the terminal radicals of type III and IV either reacts with main chain radicals I and II to crosslink, or intramolecular hydrogen shifts may transform radicals III and IV into a main chain radical of type I. The two polymers gel readily at low radiation dose.

Table IV

The main difference between these two polymers is that reaction 2 occurs for PMeOMS as evidenced by the formation of p-methoxy benzene and p-methoxy-toluene. Similar reactions do not occur for PiPMS since

Table IV   Volatile γ-radiolysis products

Product	From PMeOMS	From PiPMS
CH_4	32	8
H_2O	26	0
C_2H_4	35	4.6
C_3H_4	7.3	7.2
C_3H_6	15.2	21.2
C_3H_8	68.7	108
C_4H_{10}	8.2	57.4
CH_3OH	24.2	0
C_6H_5OH	63.8	0
$C_6H_5OCH_3$	38.6	0
$CH_3C_6H_4OCH_3$	19.6	0

neither cumene nor p-isopropyltoluene were detected after radiolysis.

Acknowledgement

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Figure Captions

Figure 1. Variation of $\overline{M}_n^{-1}$ (o) and $\overline{M}_w^{-1}$ (•) *versus* dose for PMS. Lines are least square fit of data.

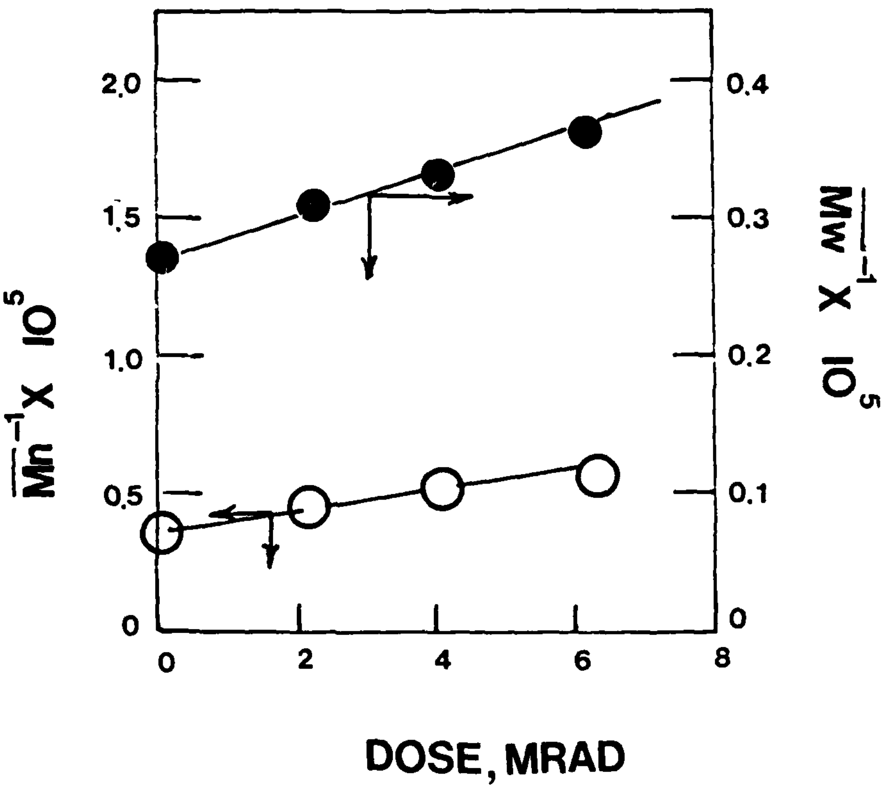
Figure 2. Variation of $\overline{M}_n^{-1}$ (o) and $\overline{M}_w^{-1}$ (•) *versus* dose: (*a*) PFMS (i); (*b*) PFMS (ii). Lines are least square fit of data.

Figure 3. Variation of $\overline{M}_n^{-1}$ (o) and $\overline{M}_w^{-1}$ (•) *versus* dose: (*a*) PCMS (ii); (*b*) PCMS (i). Lines are least square fit of data.

Figure 4. Variation of $\overline{M}_n^{-1}$ (o) and $\overline{M}_w^{-1}$ (•) *versus* dose for PBMS. lines are least square fit of data.

Figure 5. ESR spectra of γ-irradiated. (*a*) PMS; (*b*) PFMS; (*c*) PCMS; (*d*) PBMS.

Figure 6. Variation of ESR intensity with temperature: (■) PMS; (●) PFMS; (△) PBMS.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1.0
0.5
0
0.4
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0.2
0.1
0
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2
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$\overline{Mn}^{-1}$ X 10^5
$\overline{Mw}^{-1}$ X 10^5
DOSE, MRAD

Fig. 1

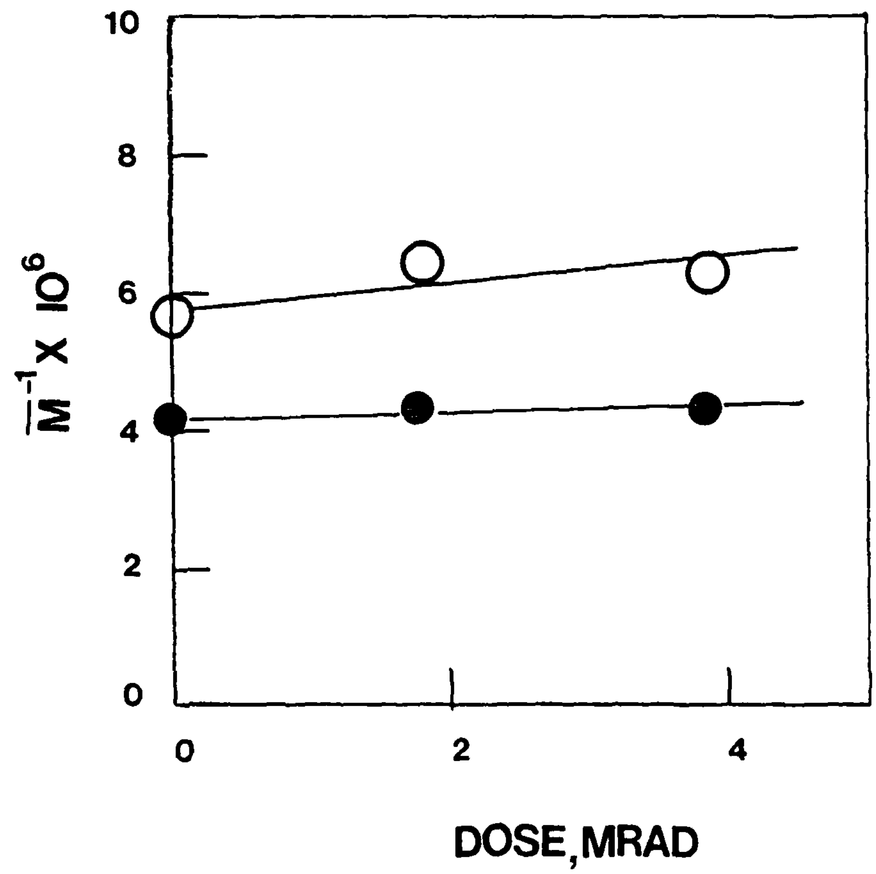
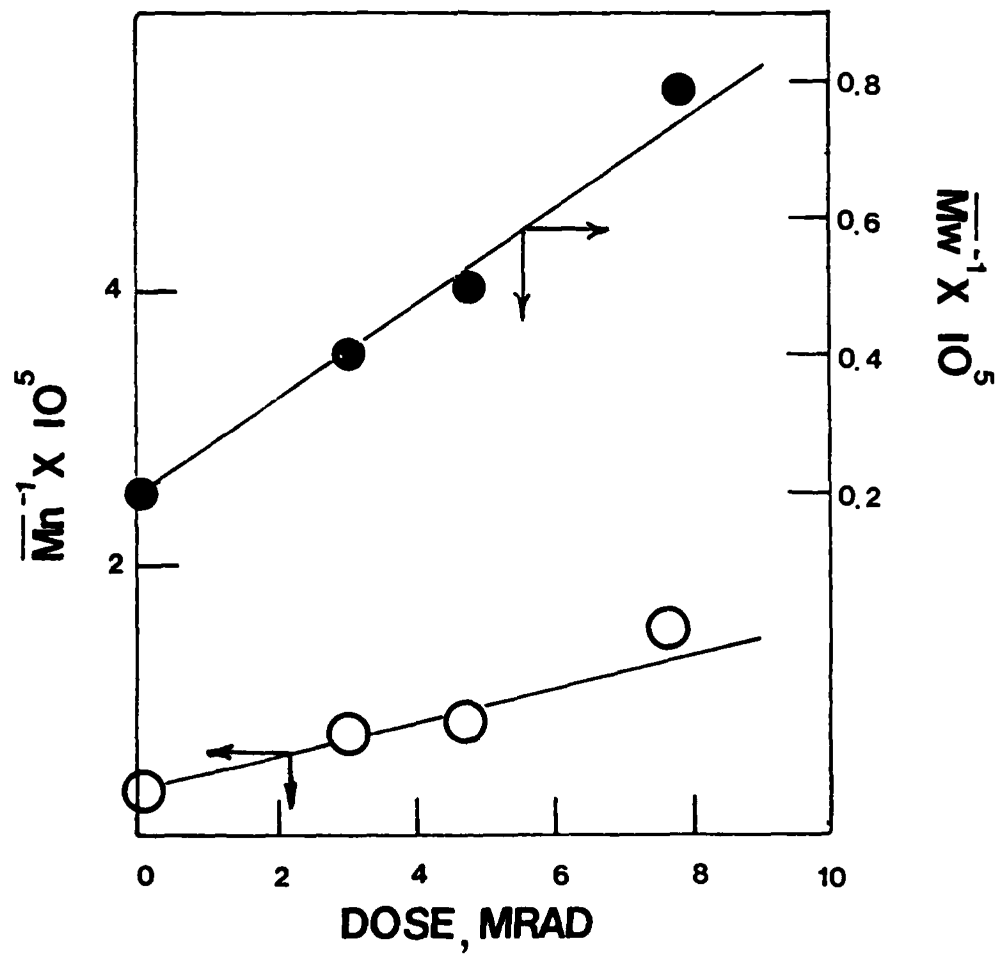


Fig.2a



$\overline{Mn}^{-1}$ X 10^5
$\overline{Mw}^{-1}$ X 10^5
4
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0.8
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0.4
0.2
0
2
4
6
8
10
DOSE, MRAD

Fig. 2b

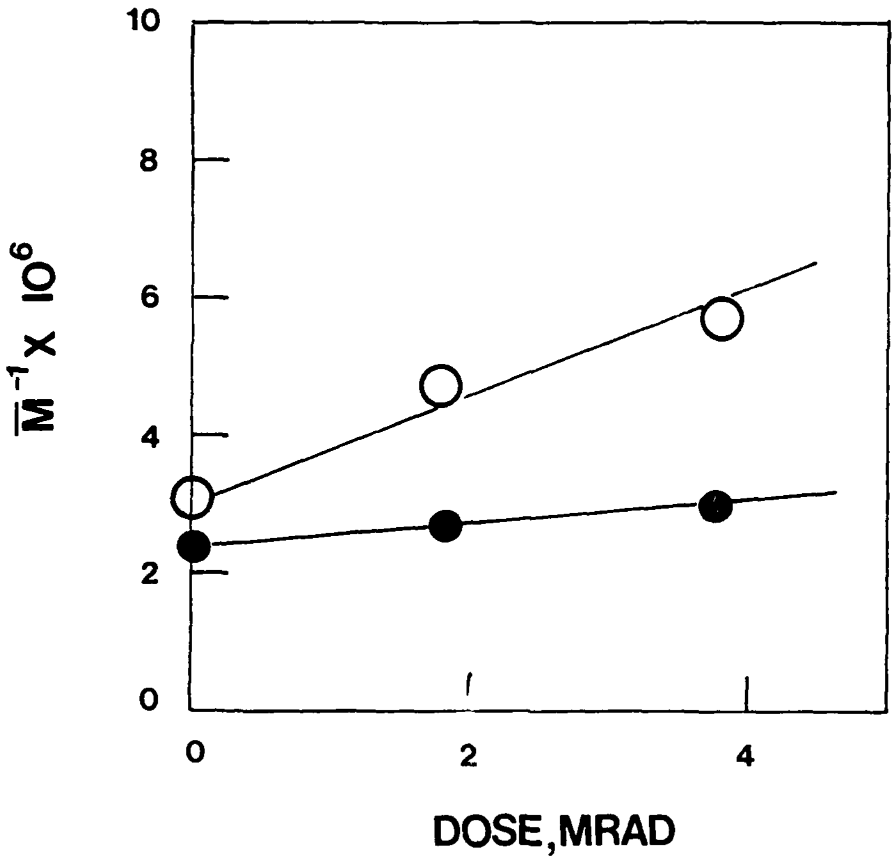

Fig.3a

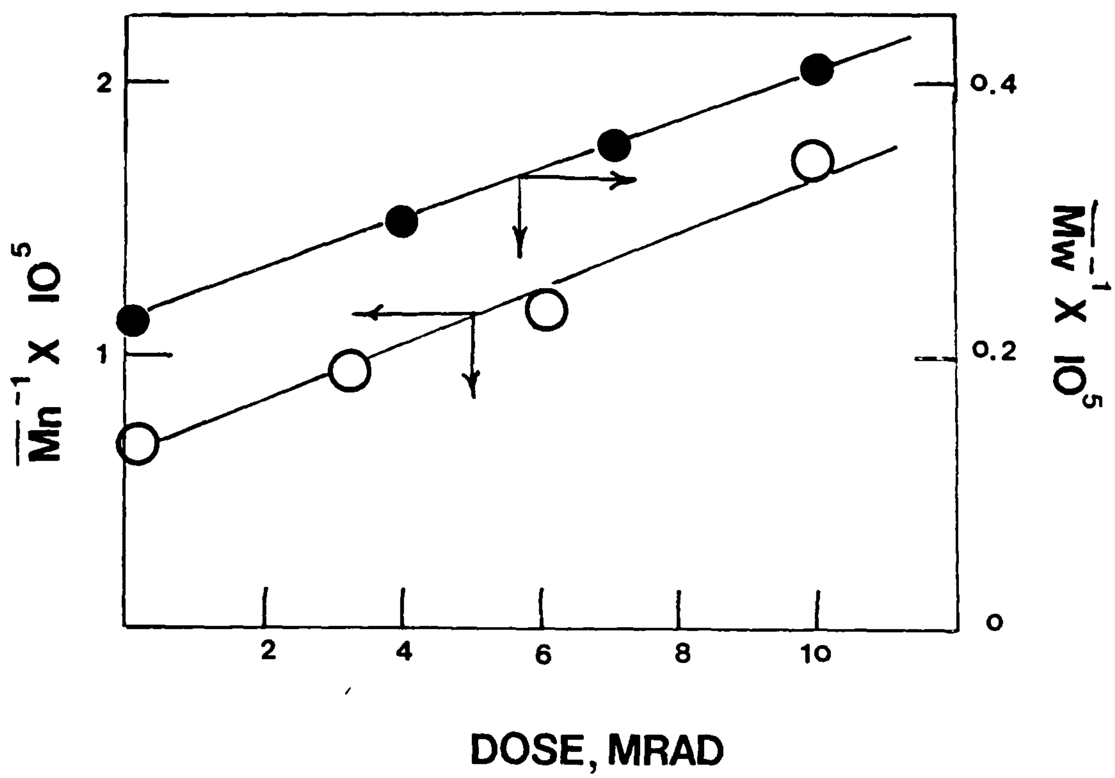

Fig. 3b

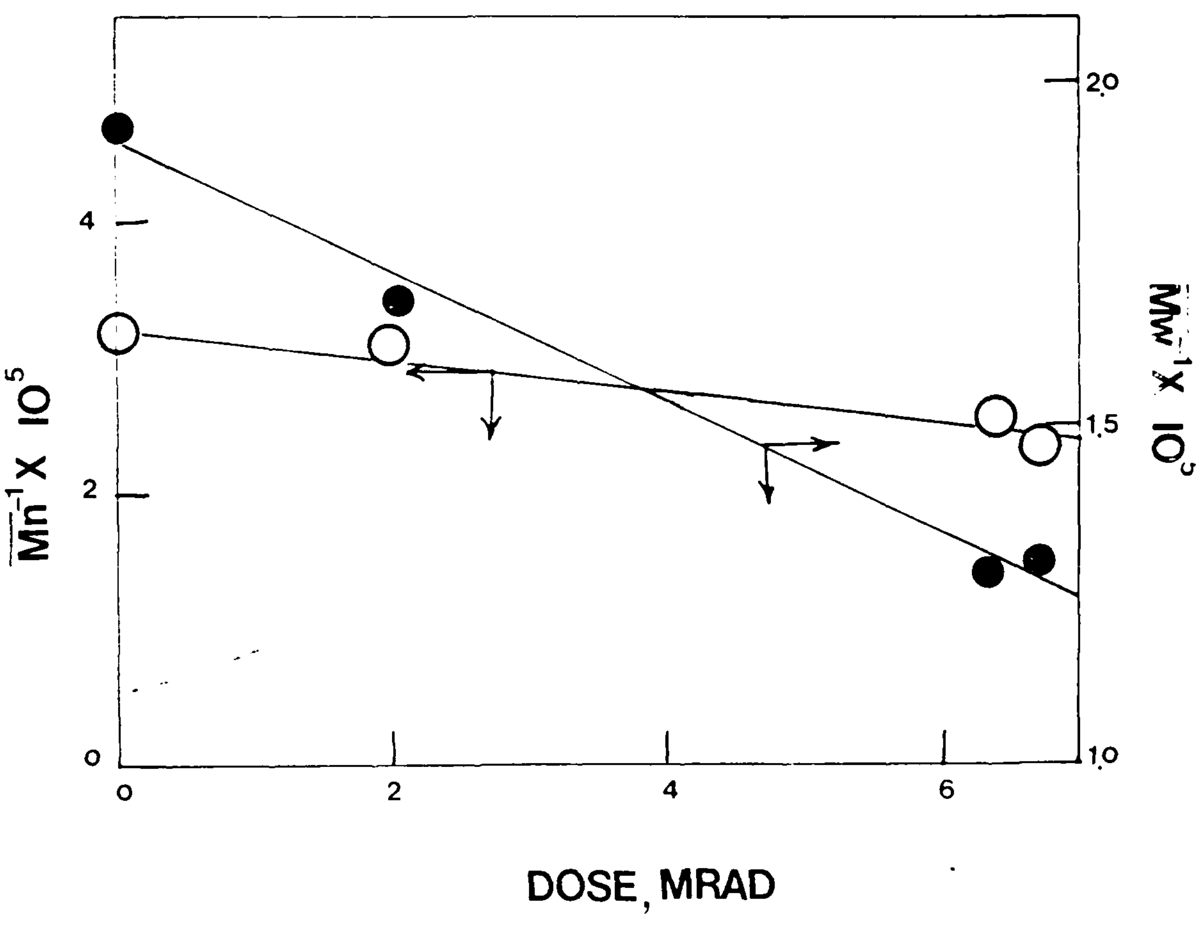

Fig.4

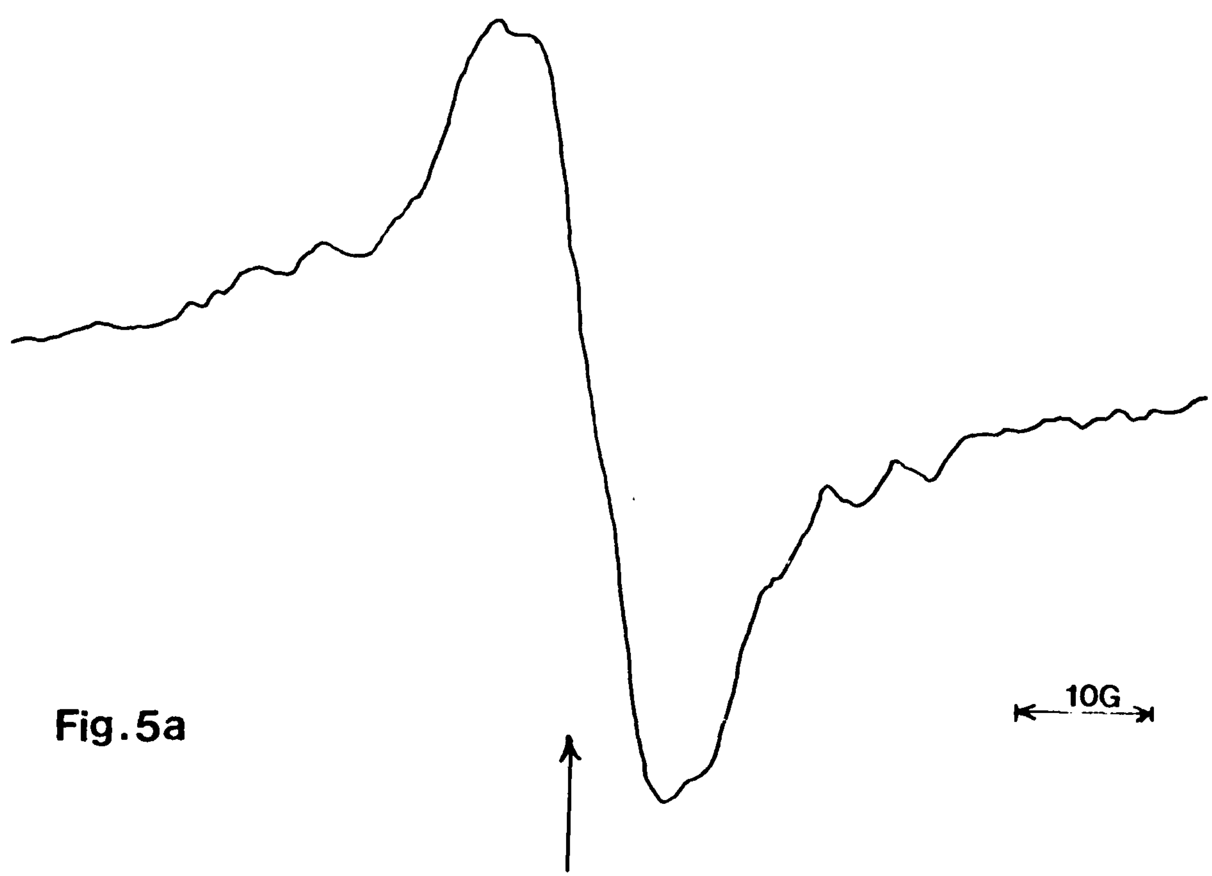

Fig.5a

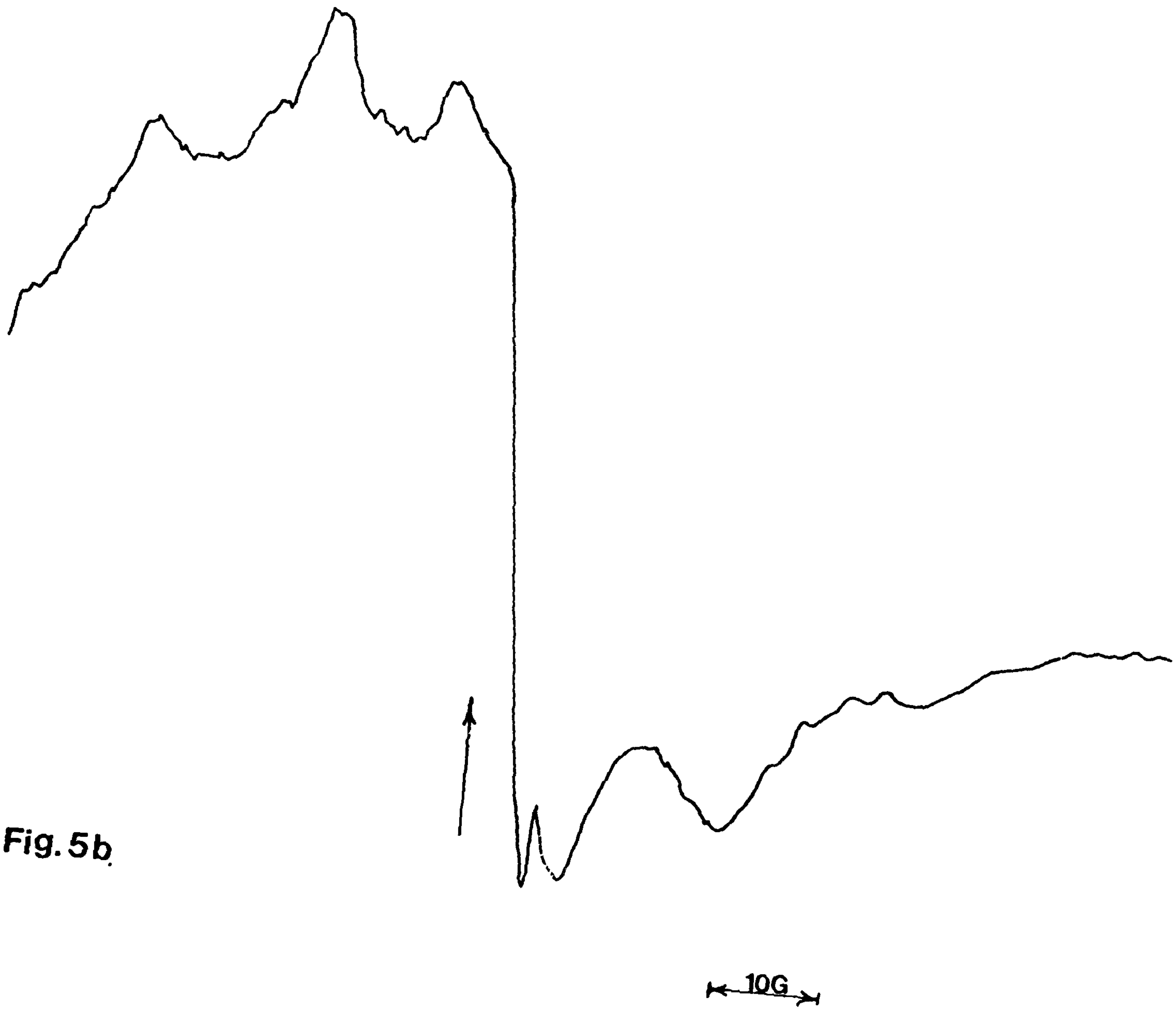

Fig. 5b

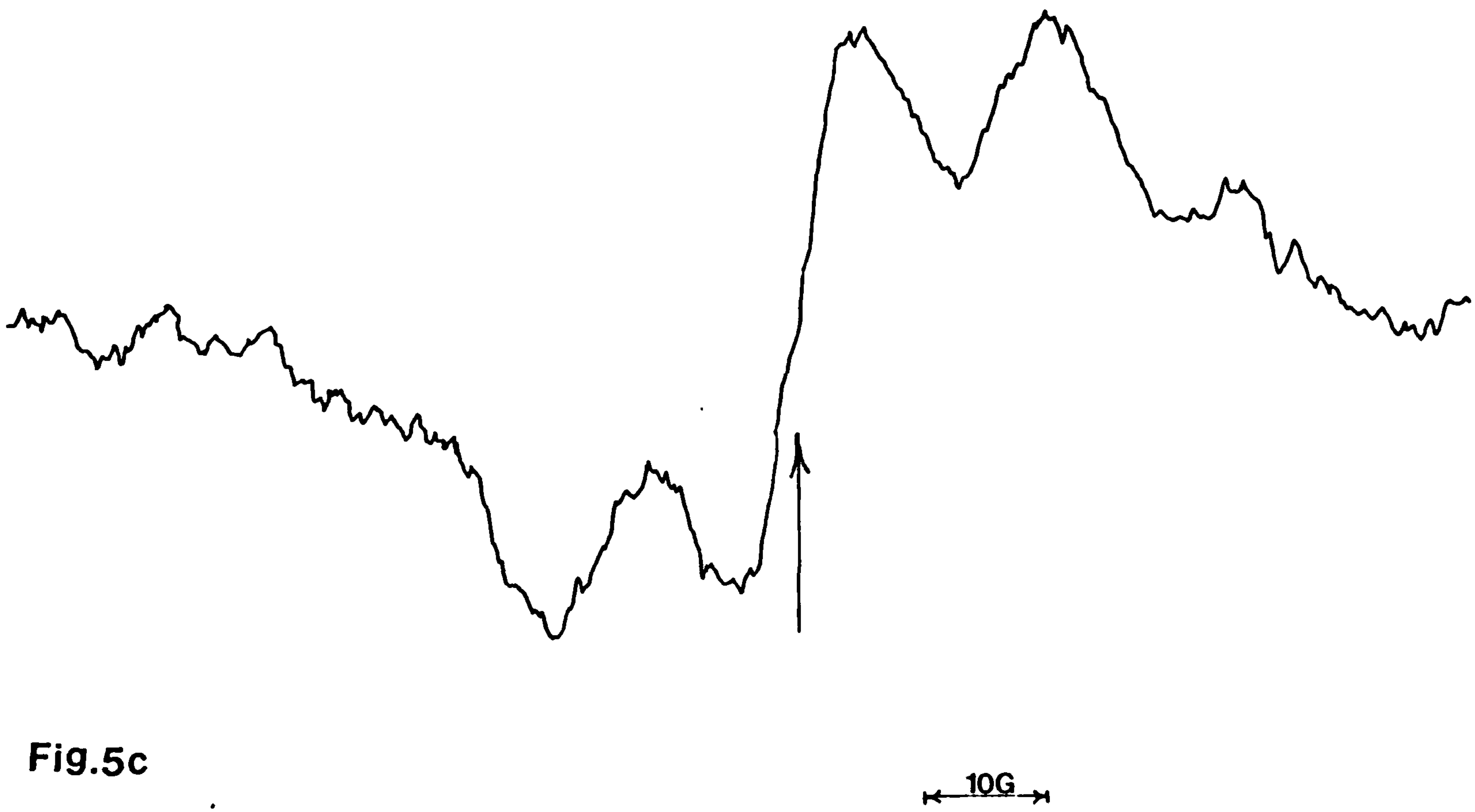

Fig.5c

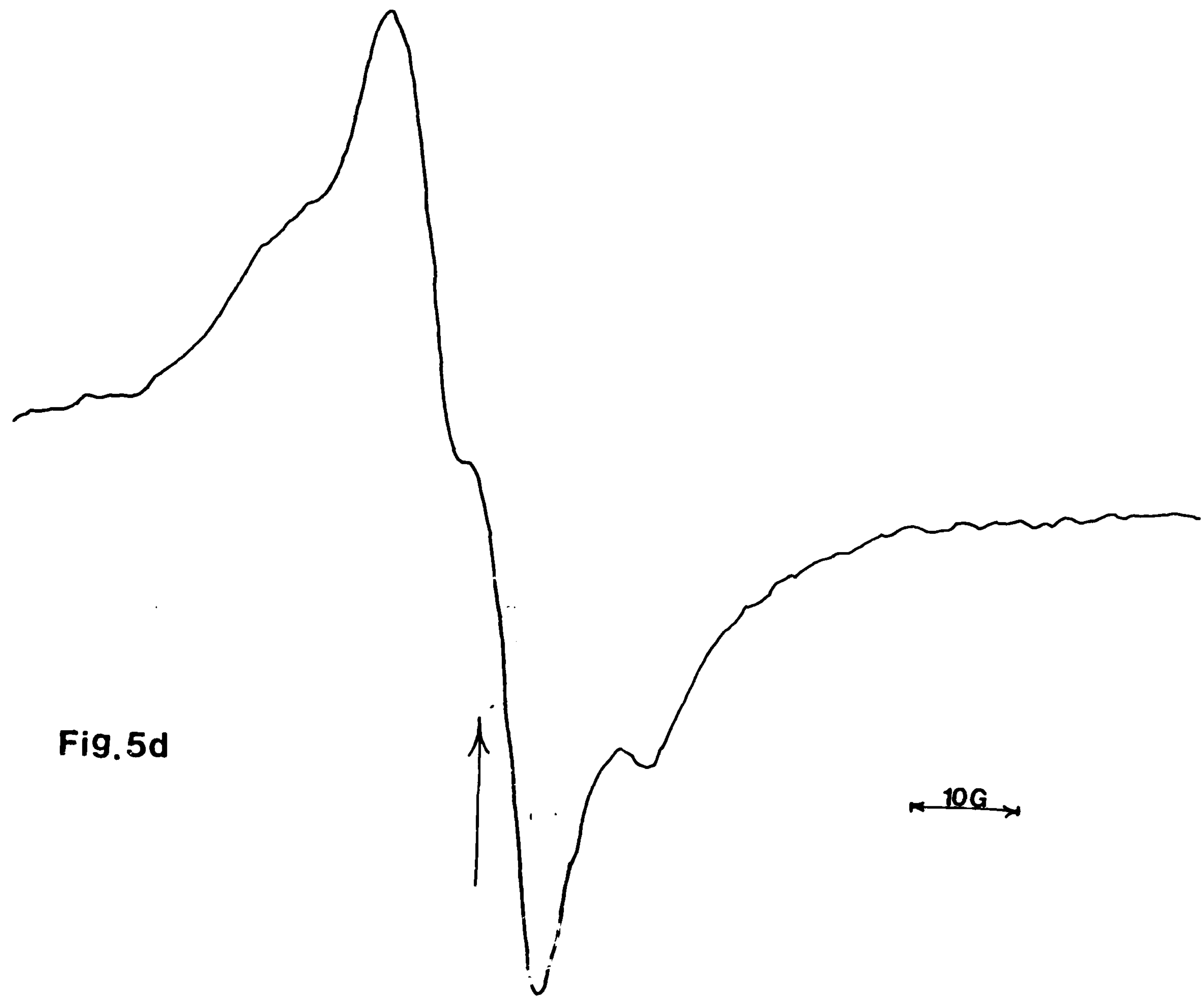

Fig. 5d

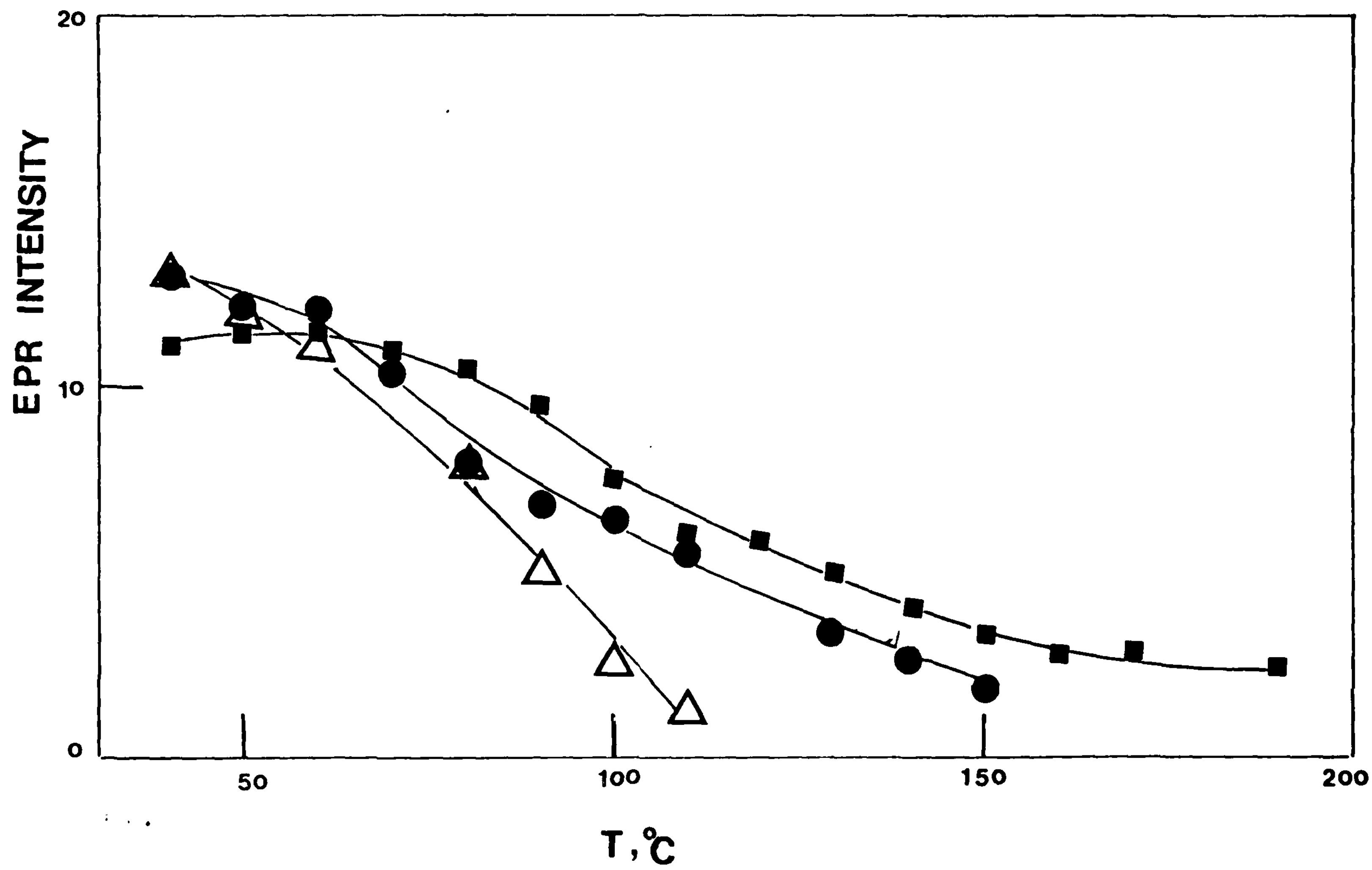

Fig.6

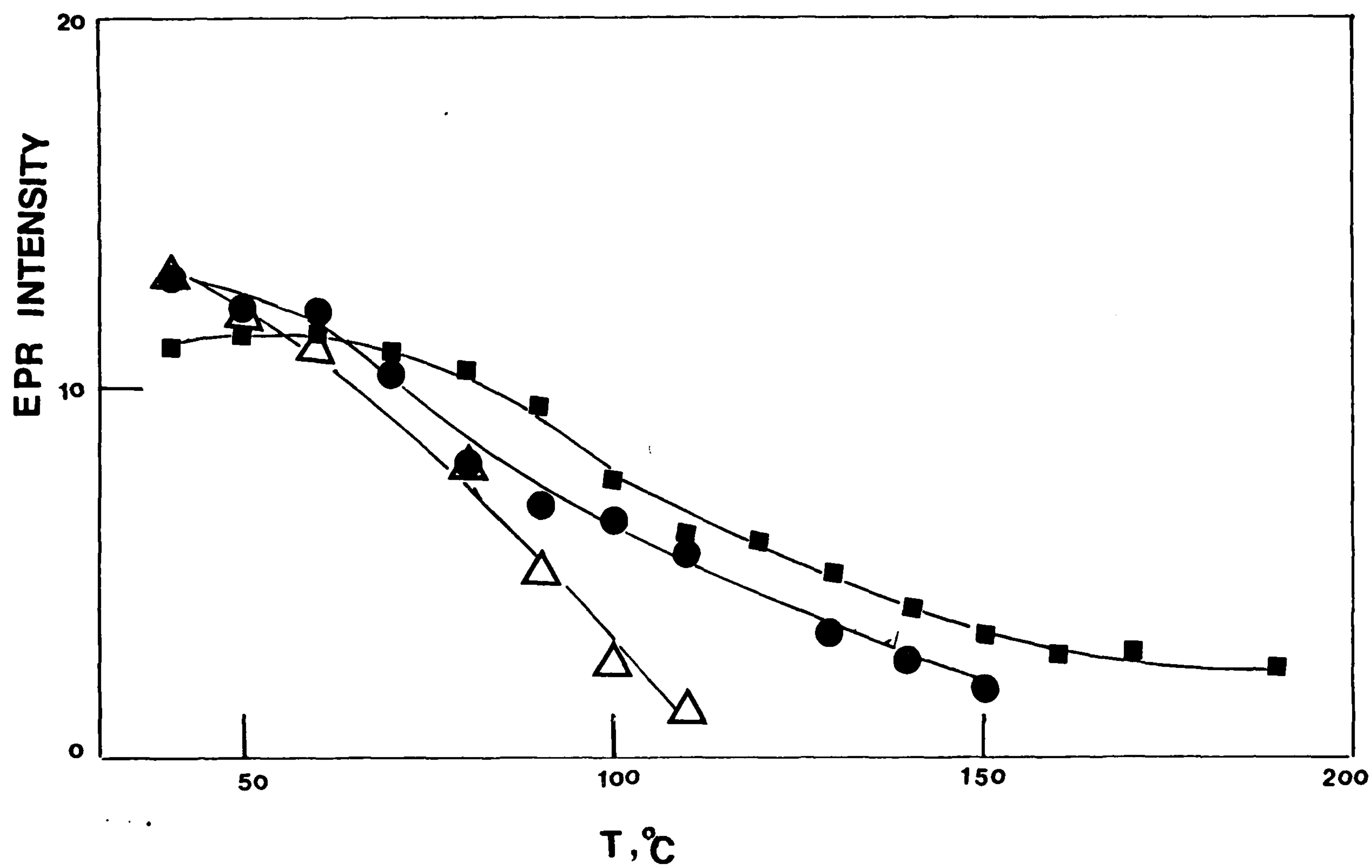

Fig.6

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